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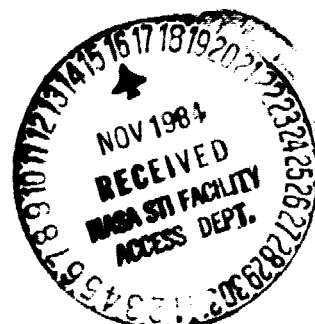
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November 1, 1984

**HIGH PRESSURE COSMOCHEMISTRY APPLIED TO
MAJOR PLANETARY INTERIORS: EXPERIMENTAL STUDIES****Investigators**

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**SUMMARY**

The overall objective of this project is to determine the properties and boundaries of high pressure phases of the H_2 -He- H_2O - NH_3 - CH_4 system that are needed to constrain theoretical models of the interiors of the major planets. This project is one of the first attempts to measure phase equilibria in binary fluid-solid systems in diamond anvil cells and, in that respect, represents a major advance of the art of high-pressure experimentation. Vibrational spectroscopy, direct visual observations, and x-ray diffraction crystallography of materials confined in externally heated cells are our primary experimental probes. We also are measuring adiabats of these materials in order to constrain models of heat flow in these bodies and to detect phase transitions by thermal anomalies.

Our initial efforts involve the NH_3 - H_2O binary. This system is especially relevant to models for surface reconstruction of the icy satellites of Jupiter and Saturn. It also is relatively easy to handle and helps us to identify technical problems so that we can solve them before we add more volatile components. During the period covered by this report (4/84-11/84), the thermal analysis experiments were completed for the P-X space, $P < 4\text{ GPa}$; $0 \leq X \leq 0.50$, near room temperature. The cryostat, sample handling equipment, and optics needed to extend the optical P-T-X work below room temperature was completed. A new, high resolution microscope was acquired for this work; and software for a new optical multi-channel analyzer that we will use to speed up pressure measurements was modified for our computer system. We also collaborated in a series of demonstration experiments to extend our spectroscopic capabilities to the shock-pressure regime that is appropriate to the interiors of Jupiter and Saturn. These experiments demonstrated that we can detect molecular fragments produced by shock-induced decomposition.

(NASA-CR-174032) HIGH PRESSURE
COSMOCHEMISTRY APPLIED TO MAJOR PLANETARY
INTERIORS: EXPERIMENTAL STUDIES Status
Report (California Univ.) 12 p
HC A02/MF A01

N85-11958

Unclas
CSCL 03B G3/91 24314

Detailed Description of Work in Progress During the Period 4/1/84-10/31/84

Ms. Koumvakalis's measurements of melting of 1:1 $\text{NH}_3\text{-H}_2\text{O}$ and Dr. Johnson's work on $(\text{NH}_3)_x(\text{H}_2\text{O})_{1-x}$ compositions in the range $0 \leq x \leq 0.3$, at pressures up to 4 GPa at room temperature ($20 \pm 2^\circ \text{C}$) have been described in previous reports. These measurements and a preliminary phase diagram based upon these data and Dr. Boehler's first thermal analysis measurements were described at several scientific conferences.

Subsequent thermal experiments caused us to rethink the preliminary phase diagram since, at some compositions, the ice VI-liquid field appeared to extend further into the liquid region and the dihydrate:liquid field further into the solid region than Dr. Johnson found. Detailed analyses of both sets of results showed that some apparent differences resulted from nucleation problems. Ice VI is especially difficult to nucleate; thus, liquid, ice VII, and, possibly, glassy solids tend to occur metastably in the ice VI field. This nucleation problem is not simply limited to this laboratory; both Yamamoto [Jpn. J. Appl. Phys. 19, (1980) 1841] and Piermarini et al. [IX AIRAPT Conf. High Pressure Res. Abstracts, (1983) AF2-1] have described the metastable liquid-ice VII equilibrium in the ice VI stability field.

Other difficulties arose because observations of "phase changes" in diamond cells and piston-cylinder studies are sensitive to different phenomena. The first crystals that are seen to precipitate from aqueous ammonia in a diamond cell only change the slope of a plot of $(dT/dP)_S$ vs. P and, thus, be overlooked in the thermal experiments. Changes of the macroscopic appearances of crystals are not always indications of phase transitions. Since the sample in a piston-cylinder apparatus cannot be seen, phases must be identified by inference; thus, at the compression rates of the order to 10 MPa/sec, glassy phases may form but be misidentified as crystalline solids.

Analysis of all of the available data led us to modify the phase diagram slightly as shown in Figure 3 of the attached manuscript. At compositions accessible with reagent grade ammonium hydroxide, the diagram includes the following phases:

- Liquid
- Liquid and dihydrate (at or below 1.0 GPa)
- Liquid and Ice VI (at 0.98 GPa)
- Dihydrate and Ice VI (at 1.5 ± 0.3 GPa)
- Dihydrate and Ice VII (at 2.1 GPa)
- Monohydrate and Ice VII (at 3.6 ± 0.2 GPa)

The manuscript describing the current status of this work appear in the proceedings of the NATO Workshop on Ice in the Solar System.

We have been working to complete the diagram. One question that still must be examined is whether the low-temperature and high-pressure hydrates are equivalent. Although there is no evidence that the mono- and dihydrate

phases observed at room temperature differ from their low-temperature counterparts, vibrational spectra or x-ray diffraction patterns are needed to identify the phases. Further experimental work needs to be done to extend the low-ammonia phase diagram to other interesting temperatures, to investigate the structures and stoichiometries of the high-pressure hydrates, and to determine the densities (and, possibly, viscosities) of the solids and fluids in the $\text{NH}_3\text{-H}_2\text{O}$ system. During the past six months, much of Dr. Johnson's time was spent in developing apparatus and techniques needed for these studies.

An appropriate variable temperature chamber for the diamond-anvil cell was assembled and successfully tested; and a new, higher resolution microscope system was purchased that we hope will eliminate many of the problems she encountered in observing minor changes (e.g., initial crystallization, disappearance of small crystals) in the samples. While waiting for delivery of the microscope, Dr. Johnson installed a new optical multi-channel analyzer system that she will use for pressure measurements. Adapters between the OMA and existing monochromators were designed and assembled, and a single-user computer program for the OMA was adapted to our multi-user lab computer system. All of these components are now working.

In related developments, the Department of Chemistry and Biochemistry has acquired a new Huber four-circle x-ray diffractometer with a cryogenic sample holder. Under aegis of a grant from the Los Alamos Division of the University of California Institute of Geophysics and Planetary Physics, we are adapting for single crystal studies at pressures to 10 GPa. The high pressure cells for this diffractometer have arrived (without the beryllium seats that should be available in early 1985), and we are adapting them to the diffractometer and testing loading procedures. When the beryllium seats are available, we will begin diffraction studies of some $\text{NH}_3\text{-H}_2\text{O}$ phases.

The department also has purchased a new FT infrared spectrometer which will arrive during the Summer but, because of software problems, was not operational until the Fall. The instrument is located adjacent to our laboratory and is regularly available for our use. Mr. Steven Boone, a second-year graduate student in the group, is working on adapting this instrument for our high pressure cells.

The Livermore Division of the University of California Institute of Geophysics and Planetary Physics is supporting a cooperative project to detect molecular emission spectra from shocked materials at very high pressures. For experimental convenience, benzene is being used for the feasibility studies. While she has had to wait upon the machine shop or outside vendors, Dr. Johnson has been involved in the project. During the last week of October, we had a week at the Livermore two-stage gas gun and succeeded in obtaining spectra of shocked benzene (at about 50 GPa and 5000 K) which clearly show molecular emission and absorption bands superimposed upon a grey-body emission. These results are now being analyzed. Another brief experimental period is tentatively scheduled for early February. When the technical problems are solved, we intend to examine methane, carbon

monoxide, nitrogen, and other light molecules of planetary interest that appear to dissociate at pressures and temperatures typical of the interiors of the major planets.

Personnel

Ms. Andrea Schwake Koumvakalis initiated most of the experimental work on this project before she began graduate work in the Department of Chemistry and Biochemistry during September 1982. Since then, she has had to devote much of her attention to courses and other degree requirements. She passed her oral qualifying exam in early June and, for the Summer, resumed her phase diagram work. During September, however, she had a son and began six-months maternity leave. Andrea will resume graduate studies during Spring 1985.

Dr. Mary Johnson continues her active involvement in the H_2O-NH_3 phase equilibria studies. Dr. Johnson obtained many of the new results reported here and, at the same time, has been testing modifications of this equipment needed to extend the work to other compositions, temperatures, and pressures and to increase the rate of data collection. She also has been our lead experimenter for the optical shock-wave work that is done in collaboration with the shock-wave physics group at Lawrence Livermore National Laboratory.

Bibliographic Data

M. L. Johnson, A Schwake, and M. Nicol, "Partial Phase Diagram for the NH_3-H_2O System: The Water-Rich Region" in J. Klinger, ed., *Proceedings of the NATO Workshop on Ices in the Solar System* (Reidel, Dordrecht, 1984). enclosed.)

PARTIAL PHASE DIAGRAM FOR THE SYSTEM $\text{NH}_3\text{-H}_2\text{O}$: THE WATER-RICH REGION

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ABSTRACT. This paper describes the status of our diamond-anvil cell experiments of the $\text{NH}_3\text{-H}_2\text{O}$ P-T-X phase diagram. Two parts of the diagram are discussed: the isothermal P-X diagram of $(\text{NH}_3)_x(\text{H}_2\text{O})_{1-x}$ for $0 \leq x \leq 0.3$ and the melting line of $(\text{NH}_3)_{0.5}(\text{H}_2\text{O})_{0.5}$. Five phases were observed, including: the liquid; ice VI and ice VII (which resembled their descriptions in the literature); a high-relief apparently isotropic ammonia monohydrate phase; and a low-relief, strongly anisotropic ammonia dihydrate phase. Our interpretation of the isothermal P-X diagram has been modified by recognition that difficulty in nucleating ice VI had led us to underestimate the importance of the ice VI plus liquid and ice VI plus ammonia dihydrate fields. Some unresolved questions and directions for future studies are discussed.

1. INTRODUCTION

Ammonia and water have been proposed as major constituents of such bodies as Neptune [1], Uranus [1, 2, 3], Titan [4], and Comet Bowell [5]. Stevenson estimates the cosmic abundance of ammonia to be about 18% that of water [4]. Hence, the study of the system $\text{NH}_3\text{-H}_2\text{O}$ at various temperatures and pressures has great relevance to the understanding of the geology of bodies in the solar system. The P-T diagram of water has been examined by a number of investigators, most recently by Mishima and Endo [6]; and Mills et al. [7] have determined the corresponding diagram for NH_3 .

The ammonia-water system at atmospheric pressure has been explored by Rollet and Vuillard [8]. Their results are shown in Figure 1. They found that $\text{NH}_3 \cdot 2\text{H}_2\text{O}$ (ammonia dihydrate, D) melts incongruently and that $\text{NH}_3 \cdot \text{H}_2\text{O}$ (ammonia monohydrate, M), which is nonstoichiometric, melts at a significantly higher temperature than the dihydrate.

This paper is a progress report that describes our work on the phase diagram of the $\text{NH}_3\text{-H}_2\text{O}$ system, our current interpretation of the available data, and additional studies that we intend to pursue. We describe experimental studies of phase boundaries in the water-rich region of the isothermal P-X diagram at room temperature and an

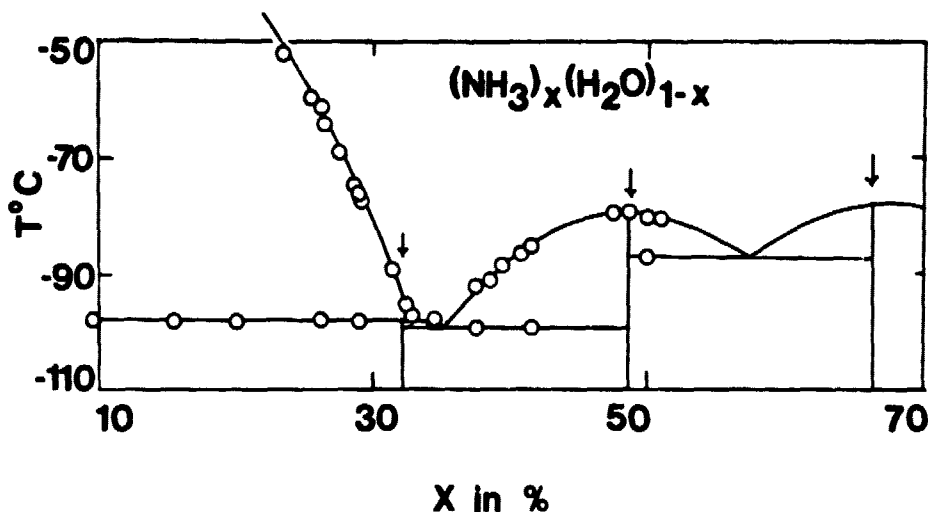


Figure 1. Part of the T-X phase diagram for the ammonia-water system at atmospheric pressure, from [8]. Arrows indicate the solid phases: ammonia dihydrate, ammonia hydrate, and ammonia hemihydrate.

approximate melting curve for the monohydrate composition. A tentative interpretation of these observations has been reported elsewhere [9,10]; however, recent experiments by Boehler [11] demonstrate that the earlier interpretation must be modified because liquid and ice VII and, possibly, glassy solids may occur metastably in the ice VI field.

2. MATERIALS AND METHODS

Two sets of experiments have been performed. In the first, the phases present were determined as a function of pressure in mixtures of several compositions up to 30 mole percent NH₃ at room temperature, $21 \pm 20^\circ\text{C}$; in the second, the solid-liquid boundary for the composition, (NH₃)_{0.5}(H₂O)_{0.5}, was monitored at several temperatures and pressures. For both sets of experiments, the samples were enclosed in a diamond-anvil high pressure cell of Holzapfel's design [12]; and phase transitions were observed visually while the pressure and/or temperature was cycled. The ruby-luminescence method [13] was used to determine the pressure.

For the first set of experiments, each sample was prepared by mixing distilled water with reagent ammonium hydroxide (Mallinkrodt Analytical Reagent) and was loaded as a liquid into the diamond cell. Concentrations were measured with a hydrometer, which had been calibrated against titration with standard acid. All phases were identified optically under polarized light.

In the second set of experiments, samples were prepared by partially crystallizing approximately equimolar mixtures of distilled water and liquid ammonia (Air Products Co., 99.99% pure) at low temperatures and decanting the supernatant liquids. Titration of

these samples with standard acid indicated that their NH_3 concentrations varied from 46 to 50 mole percent; effects of these variations on the observed phase boundaries are discussed below. The diamond cell was enclosed in a cryostat with which the temperature of the cell was varied from above room temperature to 120 K with a combination of resistance heating and cryogenic cooling.

3. RESULTS AND DISCUSSION

3.1. Room Temperature Studies

Our observations at room temperature are shown in Figure 2. Filled circles represent ice VII; striped circles, ice VI; hatched circles, ammonia dihydrate; stippled circles, ammonia hydrate; open circles, liquid; and halved circles, two-phase fields. Arrows adjacent to the circles indicate the direction in which the pressure had been changed immediately before the observation was made. In all cases, the phases were identified visually, usually both with and without crossed polarizers.

The ice phases resembled their descriptions in the literature [14,15]. The dihydrate phase had less relief than the liquid, was anisotropic under crossed nicols, and tended to form two networks of cracks at about a 70° angle to each other at low pressures. When squeezed above 3.3 GPa, dihydrate reconstituted into myrmekitic intergrowths of Ice VII with a higher-relief phase which appeared to be isotropic. From calculation of the area of the diamond cell occupied by the various phases, the low-pressure phase was shown to have a composition near $\text{NH}_3 \cdot 2\text{H}_2\text{O}$, and the high-pressure phase to have composition near $\text{NH}_3 \cdot \text{H}_2\text{O}$.

Nucleation problems complicated this work considerably, with ice VI being especially difficult to nucleate: in 24 separate measurements between 0 and 30 mole percent NH_3 where ice VI should have occurred, it was detected only 8 times, only twice at compositions other than 5 mole percent NH_3 , and never observed at the pure water composition. The points in Figure 2 labeled (a) and (b) at 10 mole percent NH_3 , and (c) at 13 mole percent NH_3 resulted from the melting of ice VII, not ice VI. A glaze of ice VI was observed during one decompression cycle as the pressure was lowered from point (d) at 10 mole percent NH_3 and 1.97 GPa; however, the pressure at which this glaze disappeared was not determined. This nucleation problem is not simply limited to this laboratory; both Yamamoto [14] and Piermarini et al. [16] have described the metastable liquid-ice VII equilibrium in the ice VI stability field.

The problems with ice VI are confirmed by Boehler's recent adiabatic compression measurements of $\text{NH}_3\text{-H}_2\text{O}$ mixtures in a piston-cylinder apparatus [11] which indicate that the ice VI-liquid field extends further into the liquid region than we found at several of the compositions described in Figure 2. In passing, we note that adiabatic compression work in a piston-cylinder apparatus is subject to other complications. The sample cannot be seen so phases must be identified by inference. Also, at the compression/decompression rates of

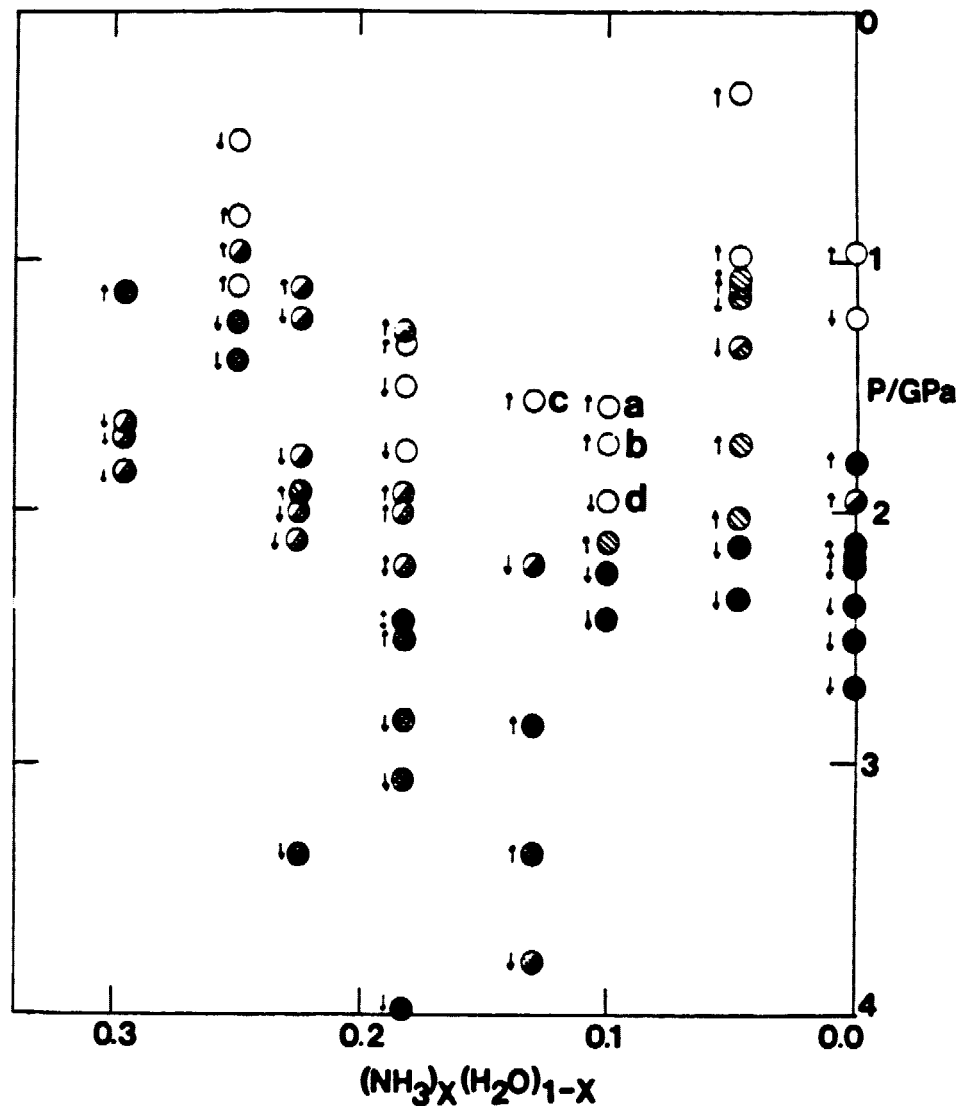


Figure 2. Our observations plotted on the isothermal P-X cut of the ammonia-water system for 21°C and mole percentages of ammonia to 0.3. The points are coded to indicate observation of liquid (open), Ice VI (diagonal shading), Ice VII (solid), ammonia dihydrate (cross-hatching), or ammonia monohydrate (dots). Two-phase observations are indicated by bisected circles, with codes for both phases indicated. The arrow next to each point indicates the direction in which the pressure had been changed just before that observation was made. Points labeled (a) through (d) are discussed in the text.

the order to 10 MPa/sec [11], glassy ammonia-bearing phases [17] rather than crystalline solids may form; compare, for instance, [18]. Therefore, the liquid-to-liquid plus ice VI transition pressures determined by Boehler should be upper limits. A combination of methods is more likely than any one technique to reveal the equilibrium phase diagram.

A phase diagram that is consistent with both sets of results is given in Figure 3. At compositions accessible with reagent grade ammonium hydroxide, the following phases were observed:

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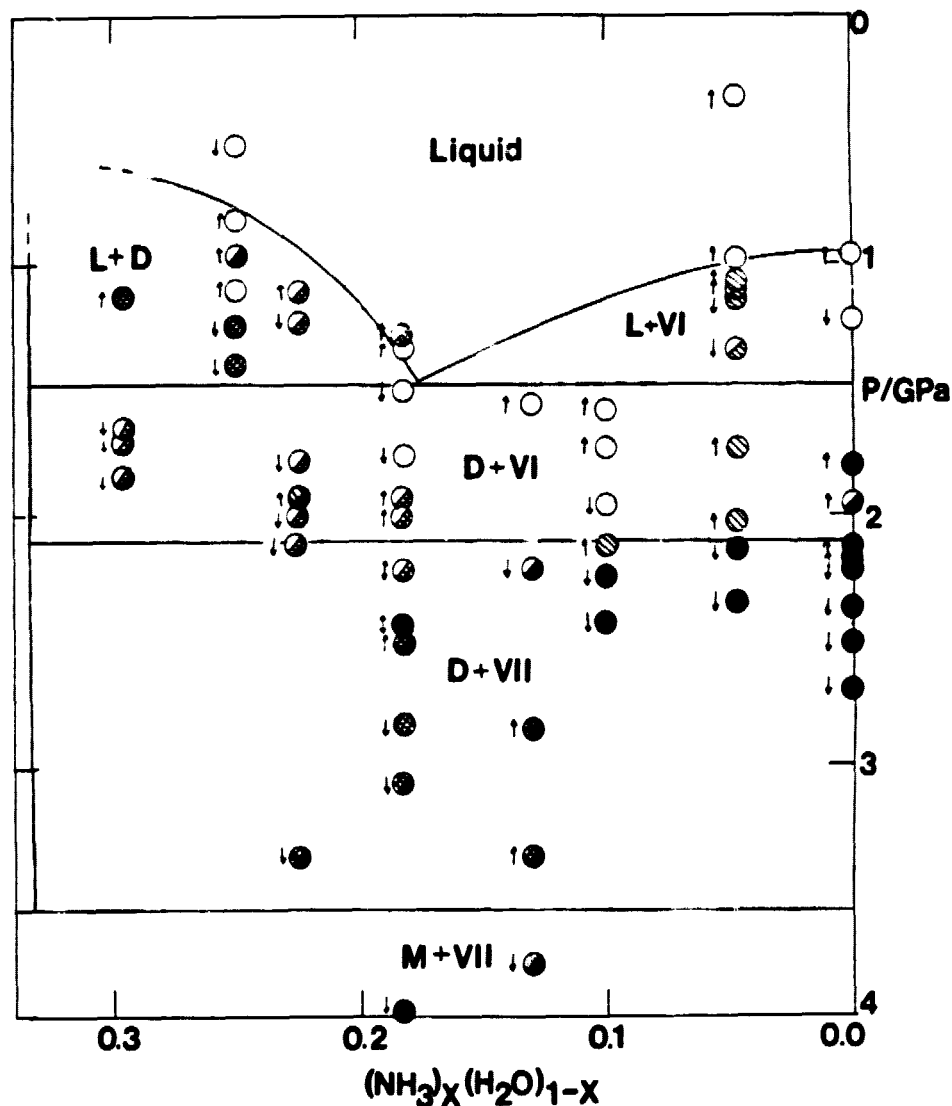


Figure 3. The revised isothermal cut of the phase diagram for the observations shown in Figure 2.

Liquid
Liquid and dihydrate (at or below 1.0 GPa)
Liquid and Ice VI (at 0.98 GPa)
Dihydrate and Ice VI (at 1.5 ± 0.3 GPa)
Dihydrate and Ice VII (at 2.1 GPa)
Monohydrate and Ice VII (at 3.6 ± 0.2 GPa)

An issue that must still be examined is whether the low-temperature and high-pressure hydrates are equivalent. Both NH_3 and H_2O have many solid phases. At low temperatures, $\text{NH}_3 \cdot \text{H}_2\text{O}$ has an orthorhombic structure [18], while the structure of $\text{NH}_3 \cdot 2\text{H}_2\text{O}$ has not been determined. Although there is no evidence that the mono- and dihydrate phases observed at room temperature differ from their low-temperature counterparts, further studies of vibrational spectra or x-ray diffraction patterns are needed to identify the phases.

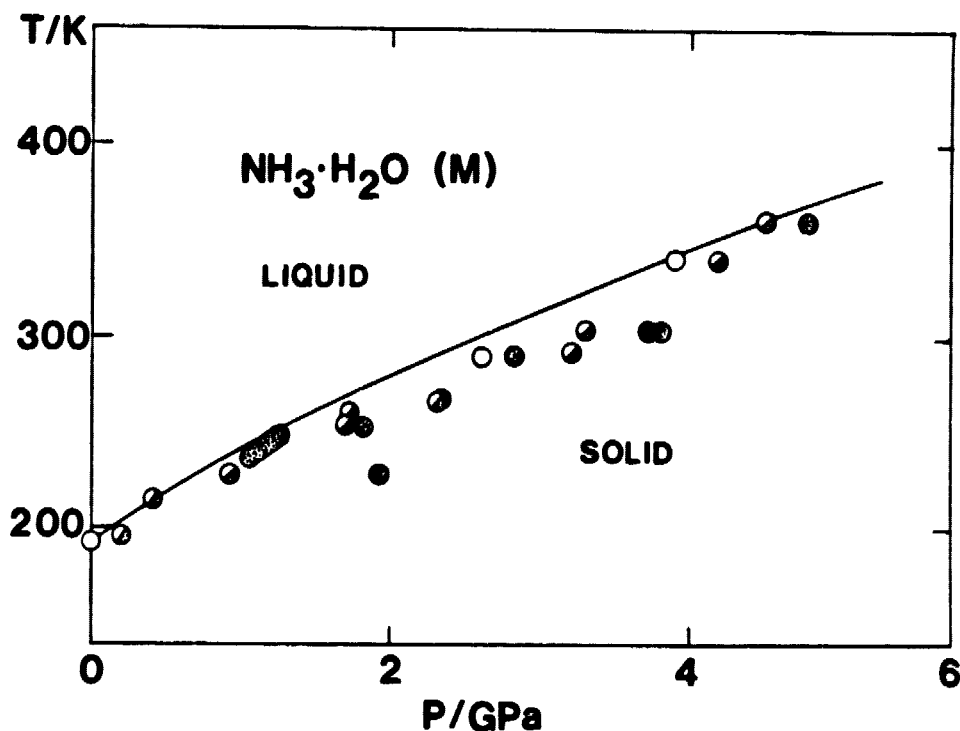


Figure 4. Melting observations for $(\text{NH}_3)_x(\text{H}_2\text{O})_{1-x}$ samples for x near 0.5 from [10]. The stippled points indicate where crystals were observed, open points show where fluid was observed, and the coexistence of fluid and solid phases is indicated by half-stippled points. If $\text{NH}_3 \cdot \text{H}_2\text{O}$ is assumed to melt congruently at all temperatures and pressures, its melting curve must lie at or above the temperatures of these two-phase points. Lower melting temperatures may occur if the monohydrate melts incongruently, as suggested by Lunine [19].

3.2. $(\text{NH}_3)_{0.5}(\text{H}_2\text{O})_{0.5}$

Our observations near this composition are shown in Figure 4. The stippled and open points indicate where the samples were solid or fluid, respectively; half-stippled points represent conditions where solid and liquid coexisted. The variable $(48 \pm 2 \text{ mole percent})$ compositions of these samples complicate the interpretation of these data. If we assume that the monohydrate melts congruently at all temperatures and pressures, the melting curve must lie at or above (higher temperatures) the two-phase points shown in this figure; however, this picture may be too simple. Lunine [19] has suggested an alternative interpretation based on the data in Figure 2: that the monohydrate melts incongruently to dihydrate plus liquid at room temperature. Further work must be done by visual methods with polarized optics, vibrational spectroscopy, or x-ray diffraction to identify the phases present.

4. SUMMARY

Although additional experimental work needs to be done, parts of the P-T-X phase diagram for the $\text{NH}_3\text{-H}_2\text{O}$ system that are consistent with all available observations have tentatively been determined in the water-rich region at room temperature and near equimolar composition at high pressures. We intend to continue our studies of this system to include:

- a. extension of the low-ammonia phase diagram to other interesting temperatures;
- b. investigation of the structures and stoichiometries of the high-pressure hydrates; and
- c. determination of the densities (and, possibly, viscosities) of the solids and fluids in the $\text{NH}_3\text{-H}_2\text{O}$ system.

ACKNOWLEDGEMENTS

We are grateful to Dr. R. Boehler for sharing his unpublished results, to Dr. J. Lunine for a copy of his calculations, and to Drs. R. Boehler, J. Lunine and D.J. Stevenson for their enlightening comments. This work was supported by NASA Grant NAGW-104.

REFERENCES

1. R. Smoluchowski (1983), The Moon and Planets 28, 137.
2. R.H. Brown, D.P. Cruikshank, and D. Morrison (1982), Nature 300, 423.
3. S. Gulkis, E.T. Olsen, and M.J. Klein (1983), Science 221, 454.
4. D.J. Stevenson, (1983), 'Interior and Surface of Titan,' in Saturn, T. Gehrels, ed., University of Arizona Press.
5. H. Campins, G.H. Rieke, and M.J. Lebofsky (1983), Nature 301, 405.
6. O. Mishima and S.J. Endo (1980), J. Chem. Phys. 73, 2454.

7. R.L. Mills, D.H. Liebenberg, and Ph. Pruzan, Ph. (1982), J. Phys. Chem. **86**, 5219.
8. A.-P. Rollet and G. Vuillard (1956), Comptes. rendus Acad. Sci. Paris **243**, 383.
9. M.L. Johnson, M. Nicol, and A. Schwake (1983), Trans. Am. Geophys. Union **64**, 875.
10. M.L. Johnson, M. Nicol, and A. Schwake (1984), Lun. Planet. Sci. XV Abstracts, 405.
11. R. Boehler (1984) [personal communication].
12. W.B. Holzapfel and R. Hirsch (1981), Rev. Sci. Instrum. **52**, 52.
13. G.J. Piermarini, S. Block, J.D. Barnett, and R.A. Forman (1975), J. Appl. Phys. **46**, 2774.
14. K. Yamamoto (1980), Jpn. J. Appl. Phys. **19**, 1841.
15. L.S. Whatley and A. vanValkenburg (1967), in Advances in High Pressure Research, R.S. Bradley, ed., (Academic Press, London), **1**, 327.
16. G.J. Piermarini, R.G. Munro, and S. Block (1983) IX AIRAPT Conf. High Pressure Res. Abstracts, AF2-1.
17. P.H.G. vanKasteren (1973), Bull. Inst. Int. Froid Annexe **4**, 81.
18. T. Wada, F. Kimura, and Y. Matsuo (1983), Bull. Chem. Soc. Jpn. **56**, 3827.
19. J. Lunine (1984) [personal communication].
20. I. Olovsson and D.H. Templeton (1959), Acta Cryst. **12**, 827.